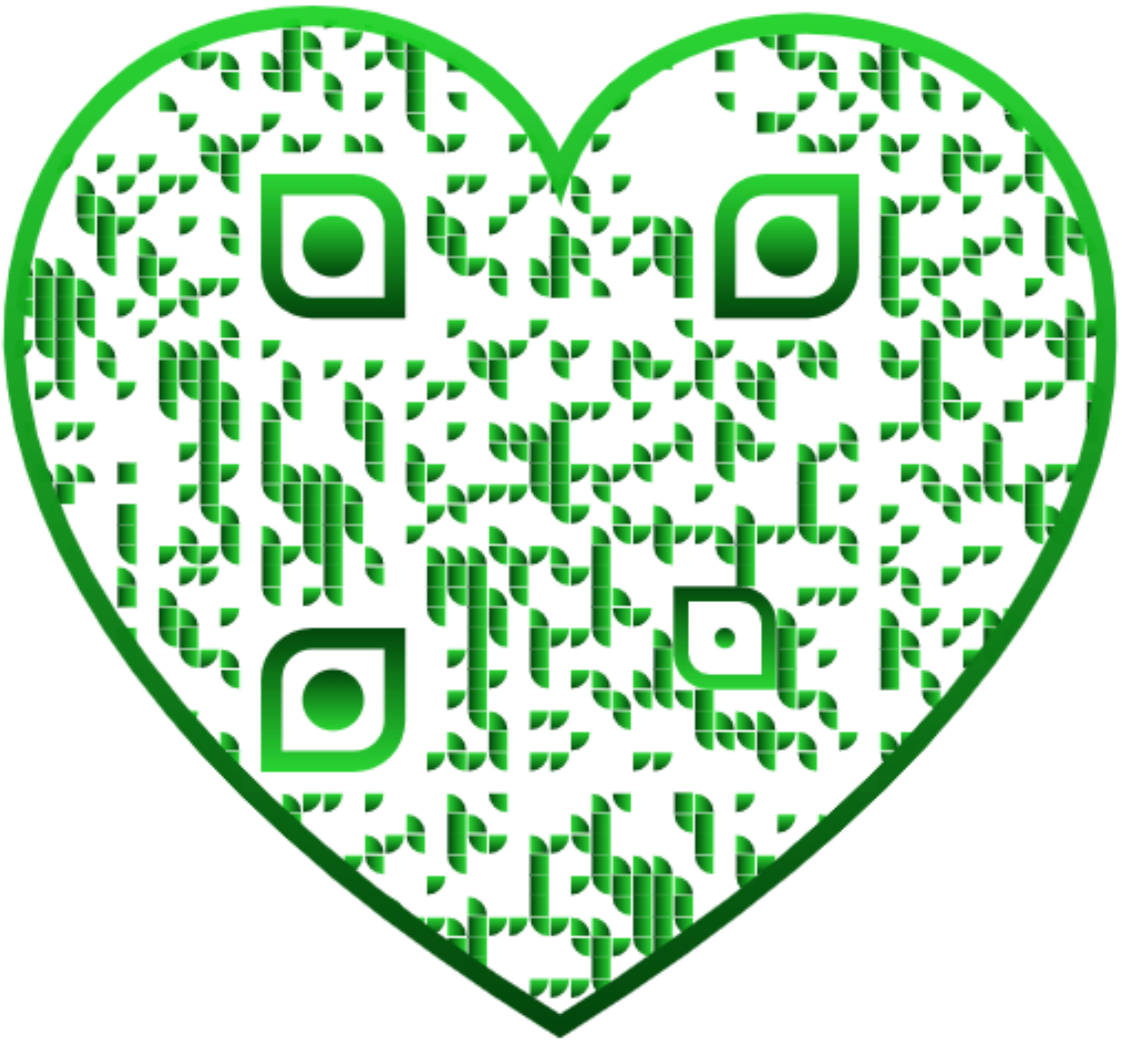
Gravimetric Methods of Analysis



objectives

- After completing this lesson, you are expected to
  - Describe the principle of gravimetry
  - Understand d/f types of gravimetric methods
  - Identify the steps followed in gravimetry
  - Use gravimetry for quantitative determination of pharmaceuticals

Gravimetric method of analysis

- A technique in which the amount of an analyte in a sample is determined by converting the analyte to some product
  - Mass of product can be easily measured
- The oldest analytical method
- based upon the measurement of the weight of a substance
- highly accurate and precise
- Since gravimetric analysis is an absolute measurement, it is the principal method for analyzing and preparing **primary standards**

Types of gravimetric analysis

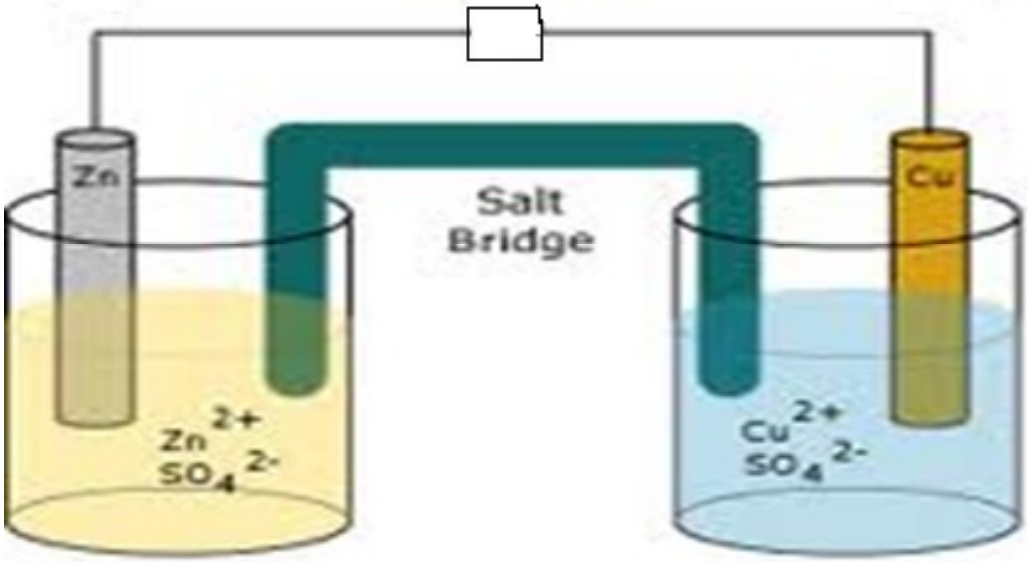
1. Electrogravimetry:

- The mass of an electrodeposit on the cathode or anode in an electrochemical cell is determined.
- The oxidation of lead, and its deposition as PbO_2 on a Pt anode
  - $Pb^{2+}(aq) + 4H2O(l) = PbO2(s) + H2(g) + 2H3O^{+}(aq)$
- The electrodeposition of Cu on a Pt cathode provides a direct analysis for Cu^{2+}
  - ➢ The difference in the electrode's mass before and after electrolysis is a direct measurement of the amount of analyte in a sample.

Brainstorming exercise

$Cu^{2+} + 2e^- \Leftrightarrow Cu(s)$ **Reduction potential= +0.337**

$Zn^{2+} + 2e^- \Leftrightarrow Zn(s)$ **Reduction potential= -0. 763**



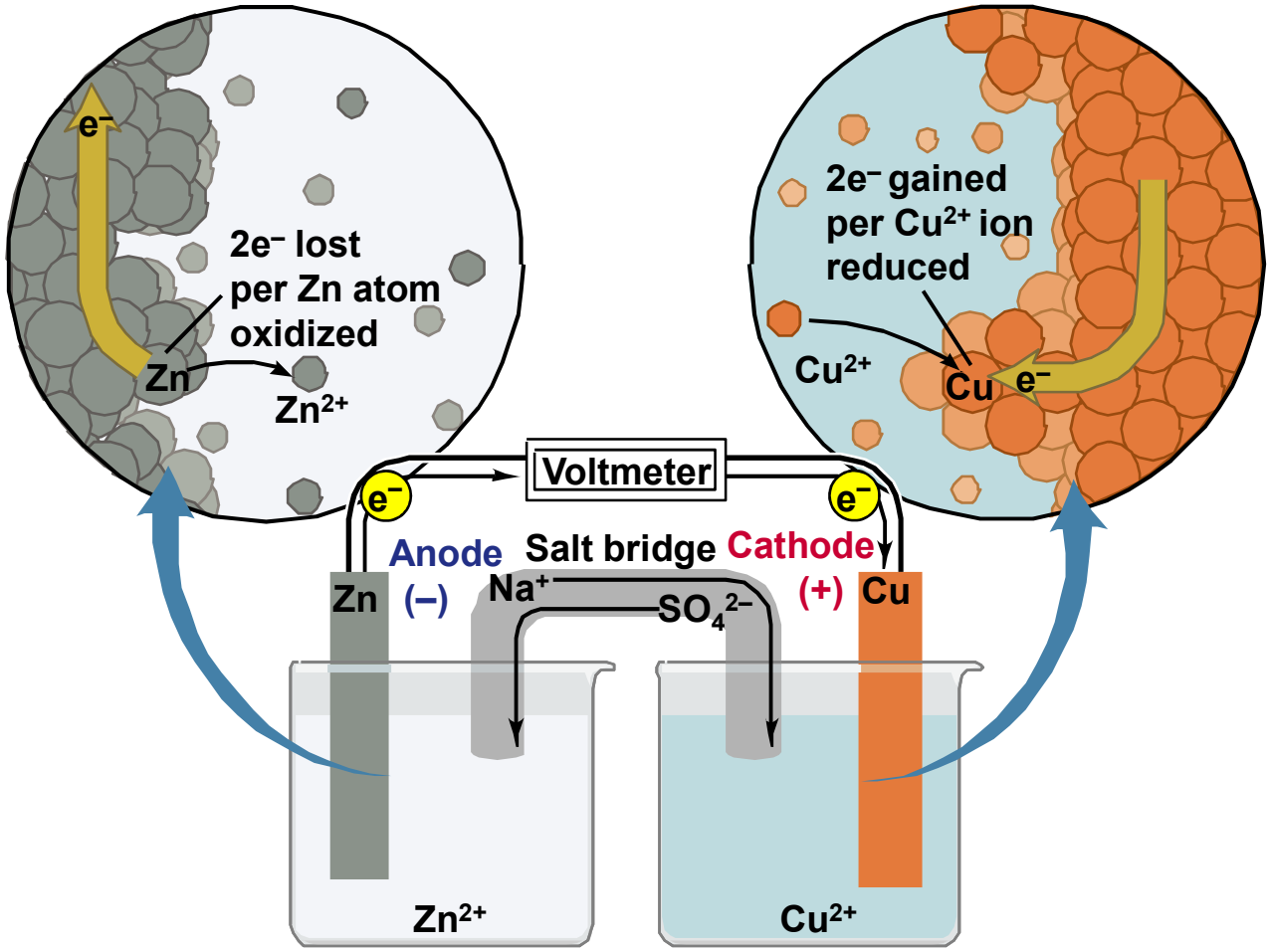
0.010M $ZnSO_4$ solution

0.010M $CuSO_4$ solution

Predict the direction of e^- flow

which is the cathode?

which is the anode?



Oxidation half-reaction

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall (cell) reaction

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

2. Particulate gravimetry:

- The mass of a particulate analyte is determined following its separation
  - Using a filtration or an extraction from its matrix.

    E.g. determination of total suspended solids

3. Precipitation Gravimetry:

- Determination is based on mass of precipitate
- e.g. determination of Cl^- by precipitating it as AgCl

4. Volatilization Gravimetry:

- When thermal or chemical energy is used to remove a volatile species
- e.g. determining moisture content using thermal energy to vaporize H_2O
- Determination of ash value (inorganic ash content)

- **Precipitation and Volatilization** are the major types of gravimetric methods.

Precipitation methods

- **Principles**:

  The analyte is converted to a insoluble ppt.

  (i) Reagent + Analyte → Solid Product (collect and measure mass)

  - Desired Properties of Solid Product
    - Should be low solubility
    - Easily filterable (i.e., large crystals)
    - Very Pure
    - Known and constant composition

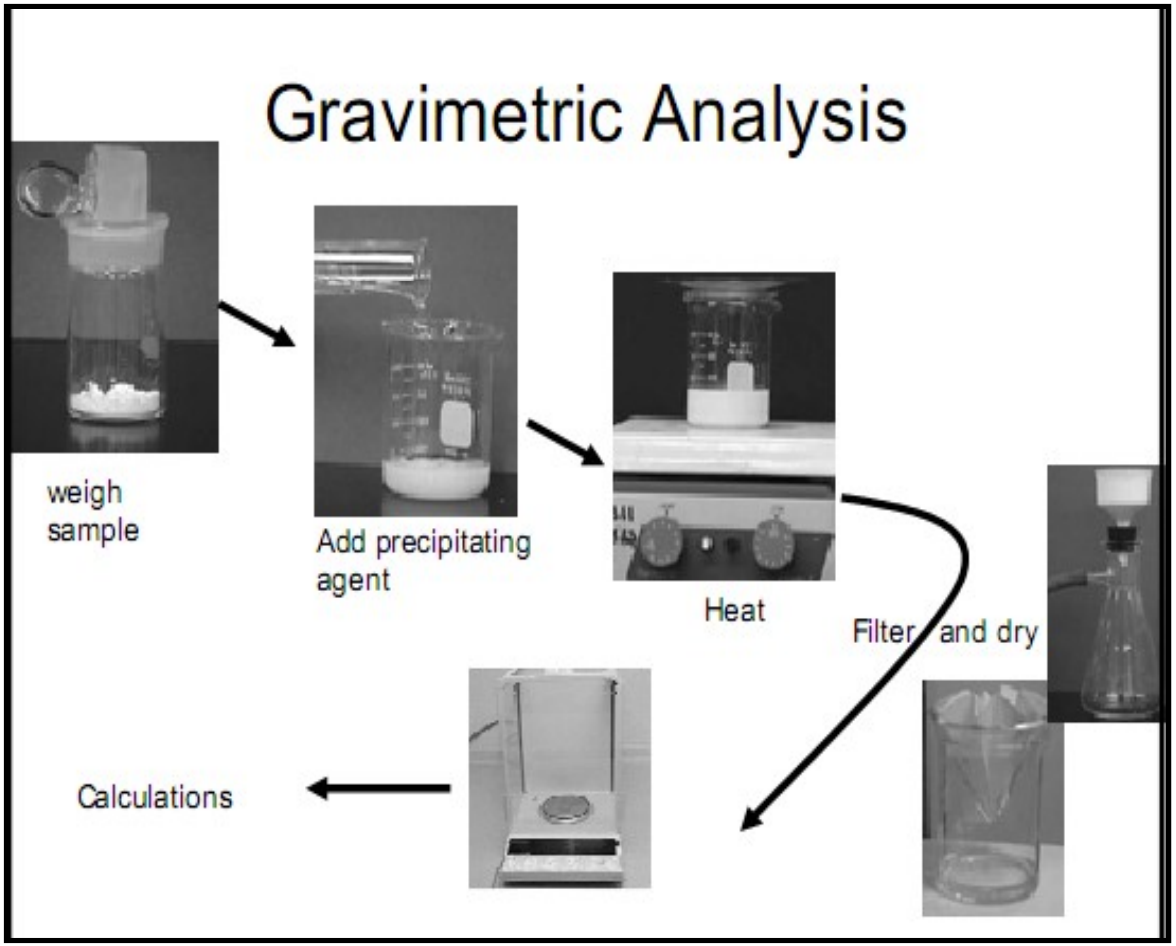
  (ii) This ppt is then filtered, washed free of impurities, and converted to a product of known composition

  - By suitable heat treatment, and the product is weighed.

Precipitation methods ….

☞ Steps in gravimetric analysis (Precipitation gravimetry)

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing
8. Calculation



1. Preparation of the solution

- Factor that must considered during preparation of sol:

  i. Volume of the solution during precipitation

  ii. The concentration range of the test substance

  iii. Temperature

  iv. pH

2. Precipitation

✍Properties of precipitating reagents

☞ Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte.

- **Specific reagents**, which are rare, react only with a single chemical species.
  - Dimethylglyoxime is a specific agent only for Ni^{2+}
- **Selective reagents**, which are more common, react with a limited number of species.
  - $AgNO_3$ is a selective agent for Cl^-, Br^-, I^-, SCN^-

Properties of good precipitates

- Easily filtered and washed free of contaminants.
- Of sufficiently low solubility

  i.e no significant loss of the analyte occurs during filtration and washing.
- Unreactive with constituents of the atmosphere
- Of known chemical composition after it is dried or, if necessary, ignited.

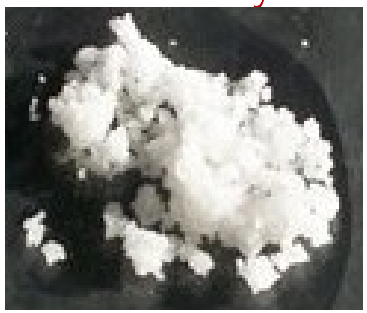
Particle size and filterability of precipitates

- Filterability:

  (i) Want product to be large enough to collect on filter:

  - Doesn't clog filter
  - Doesn't pass through filter

  (ii) Best Case: Pure Crystals



  Worst Case: Colloidal suspension

  - Difficult to filter due to small size
  - Tend to stay in solution indefinitely → suspended by Brownian motion
    - usually 1-100 nm in size

- As the particle size of the precipitate increases, the impurities decrease and the ease of filtration increases.

3. Digestion of the Precipitate

- ✓ To make precipitate become larger and more pure crystals.
- ✓ It improves the purity and crystallinity of the precipitate.
  - ✓ An important advantage of digestion is observed for colloidal precipitates where large amounts of adsorbed ions cover the huge area of the precipitate.
    - ✓ Digestion forces the small colloidal particles to agglomerate which decreases their surface area and thus adsorption.
      - ✓ **Particle size↑→ specific surface area↓→ adsorption↓**

4. Filtering and Washing the Precipitate

- Coprecipitated impurities, especially those on the surface, can be removed by washing the precipitate after filtering.
- It is crucial to wash the precipitate very well
  - **In order to remove all adsorbed species which will add to weight of precipitate.**
- Avoid using too much water since part of the precipitate may be lost.
- In colloidal ppts dil nitric acid, ammonium nitrate, or dil acetic acid may be used.
  - **Since they are volatile when heated**

5. Drying and Ignition

- The purpose of:
  - Drying (heating at about 120-150 °C in an oven) or
  - Ignition in a muffle furnace at temp ranging from 600-1200 °C
    - Is to get a material with exactly known chemical composition
      - So that the amount of analyte can be accurately determined.

6. Weighing & Calculations

- In gravimetric analysis, the percentage of the desired constituent may be achieved by the ff expression :

$$\% \text{ Analyte} = \frac{\text{Wt. of ppt' x GF}}{\text{Wt. of sample}} \text{ x } 100,$$

Wt. of ppt' - weighed gravimetrically

$$\text{GF} = \frac{\text{f. wt. analyte (g/mol)}}{\text{f. wt. ppt (g/mol)}} \times \frac{\text{a(mol analyte)}}{\text{b(mol ppt)}}$$

$$\text{GF} = \frac{\text{wt. analyte}}{\text{wt. ppt}}$$

- Gravimetric factor(GF) - the weight of analyte per unit weight of precipitate

Substances Assayed Gravimetrically

- ***E.g. 1***: Calculate % purity of NaCl
- NaCl : 0.257 g ; using 5% w/v silver nitrate
- The weight of AgCl is found to be 0.6288 g experimentally,

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

169.87 58.44 **143.22** 84.99

- solution:

$GF = 58.44/143.22 = 0.4078$

$$\%Desired = \frac{Wt.of\ ppt \times GF}{Wt.of\ sample} \times 100$$

$$\frac{0.6288 \times 0.4078}{0.257} \times 100 = 99.77\%$$

E.g.2 : The calcium in a 200.0ml sample of a natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002g. The mass of the crucible plus CaO (56.077g/mol) was 26.7134 g.

Calcualte the conc (% w/v) of Ca (40.078g/mol) in water.

$$CaC_2O_4\,(s) \xrightarrow{\Delta} CaO\,(s) + CO\,(g) + CO_2$$

$$mass\ \ CaO\ \ = 26.7134\ - 26.6002\ \ = 0.1132\ \ g$$

$$GF\ \ = 40.07\ /\ 56.077\ \ = 0.7146$$

$$\%\ \text{Desired}\ \ = \frac{\text{Wt. of ppt x GF}}{\text{Wt. of sample}}\ \text{x}\ 100$$

$$\%Ca\ \ = \frac{0.1132g\ \ \text{x}\ 0.7146}{200ml}\ \text{x}\ 100\ \ = 0.04045\ \ \%$$

Table: Pharmaceutical substances assayed gravimetrically

S.No.	Name of Substance	Qty. Prescribed	Drying Temp. (°C)	Calculations
1.	Barium sulphate	0.60 g	105	Each g of the residue ≡ 0.9213 g of $BaSO_4$
2.	Fluorescein sodium	0.50 g	105	Each g of the residue ≡ 1.132 g of $C_{20}H_{10}Na_2O_5$
3.	Piperazine adipate	0.20 g	105	Each g of the residue ≡ 0.4268 g of $C_4H_{10}N_2$. $C_6H_{10}O_4$
4.	Piperazine hydrate	0.20 g	105	Each g of the residue ≡ 0.3567 g of $C_4H_{10}N_2$. 6 H_2O
5.	Piperazine phosphate	0.20 g	105	Each g of residue ≡ 0.3382 g of $C_4H_{10}N_2$. H_3PO_4
6.	Piperazine phosphate Tabs.	0.15 g	105	Each g of the residue ≡ 0.3714 g of $C_4H_{10}N_2$. H_3PO_4. H_2O
7.	Quinalbarbitone Tablets	0.10 g	105	Each g of the residue ≡ 1.092 g of $C_{12}H_{17}N_2NaO_3$
8.	Quiniodochlor Tablets	0.10 g	105	Each g of the residue ≡ 0.91 g of C_9H_5ClNO
9.	Sodium aurothiomalate (For Na)	0.2 g	600	Each g of the residue ≡ 0.03237 g of Na
10.	Sulphobromophthalein sodium (For Sulphur)	0.2 g	600	Each g of the residue ≡ 0.1374 g of S
11.	Thiocarbazone	0.1 g	105	Each g of the residue ≡ 0.4606 g of $C_{10}H_{12}N_4OS$

- **Advantage of preciptation gravimetric analysis**:
  - Equipment needs are few (beakers, filtering devices, ovens or burners, and balances),
    - inexpensive, routinely available in most laboratories, and easy to maintain

- **Limitation:**
  - Precipitation gravimetric procedures are time-intensive; rarely practical when analyzing a large number of samples.

4. Volatilization methods

- In this method the analyte or its decomposition products are volatilized at a suitable temperature.
  - The volatile product is then collected and weighed, or, alternatively,
  - the mass of the product is determined indirectly from the loss in mass of the sample.
- The analysis depends on the removal of the volatile species from the sample:
  - **Determination of the hydrate percentage in hydrate cpds**

The end